

## **Simulated features of the air-hydrate formation process in the Antarctic ice sheet at Vostok**

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### **Abstract**

A recently developed theory of post-nucleation conversion of an air bubble to air-hydrate crystal in ice is applied to simulate two different types of air-hydrate formation in polar ice sheets. The work is focused on interpretation of the Vostok (Antarctica) ice-core data. The hydrostatic compression of bubbles is the rate-limiting step of the phase transformation which is additionally influenced by selective diffusion of the gas components from neighboring air bubbles. The latter process leads to the gas fractionation resulting in lower (higher) N<sub>2</sub>/O<sub>2</sub> ratios in air hydrates (coexisting bubbles) with respect to atmospheric air. The typical time of the post-nucleation conversion decreases at Vostok from 1300-200 a at the beginning to 50-3 a at the end of the transition zone. The model of the diffusive transport of the air constituents from air bubbles to hydrate crystals is constrained by the data of Raman spectra measurements. The oxygen and nitrogen self-diffusion (permeation) coefficients in ice are determined at 220 K as  $4.5 \times 10^{-8}$  and  $9.5 \times 10^{-8}$  mm<sup>2</sup> a<sup>-1</sup>, respectively, while the activation energy is estimated to be about 50 kJ mol<sup>-1</sup>. The gas-fractionation time-scale at Vostok, T(F) ~ 300 a, appears to be two orders of magnitude less than the typical time of the air-hydrate nucleation, T(Z) ~ 30-35 ka, and thus the condition for the extreme gas fractionation, T(F) <

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